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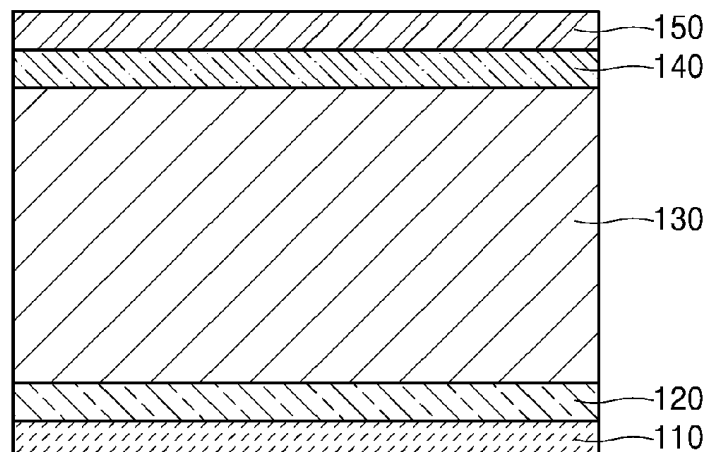
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(54) **PHOTOELECTRIC CONVERSION DEVICE INCLUDING PEROVSKITE COMPOUND, METHOD OF MANUFACTURING THE SAME, AND IMAGING DEVICE INCLUDING THE SAME**

(57) A photoelectric conversion device including a perovskite compound, a method of manufacturing the same and an imaging device comprising the same are provided.

FIG. 1

100



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Description

FIELD OF THE INVENTION

5 **[0001]** The present disclosure relates to a photoelectric conversion device including a perovskite compound, method of manufacturing the same and an imaging device including the same.

BACKGROUND OF THE INVENTION

10 **[0002]** A photoelectric conversion device refers to a device which converts an optical signal to an electrical signal. In general, a photoelectric conversion device uses photoelectric effects, for example, a photoconductive effect and a photovoltaic effect for converting an optical signal to an electrical signal.

[0003] For example, such a photoelectric conversion device may be used in an imaging device. The imaging device may include photoelectric conversion devices arranged two-dimensionally on transistors, and collect electrical signals generated from the photoelectric conversion devices.

SUMMARY OF THE INVENTION

20 **[0004]** Provided are a photoelectric conversion device including a perovskite compound, and an imaging device including the same, and more particularly, a photoelectric conversion device including a perovskite compound in an electron blocking layer and a hole blocking layer, and an imaging device including the photoelectric conversion device.

[0005] Additional aspects will be set forth in part in the description which follows and, in part, will be apparent from the description, or may be learned by practice of the presented example embodiments.

25 **[0006]** According to an aspect of an example embodiment, a photoelectric conversion device includes: a first conductive layer; a second conductive layer; a photoelectric conversion layer between the first conductive layer and the second conductive layer; an electron blocking layer between the photoelectric conversion layer and the first conductive layer; and a hole blocking layer between the photoelectric conversion layer and the second conductive layer, wherein the electron blocking layer includes a first perovskite compound represented by Formula 1, and the hole blocking layer includes a second perovskite compound represented by Formula 2:

30 <Formula 1 > $[A^1][B^1][X^1_{(3-n)}Y^1_n]$

wherein, in Formula 1,

35 A^1 is at least one monovalent organic cation, at least one monovalent inorganic cation, or any combination thereof, B^1 is at least one divalent inorganic cation, X^1 and Y^1 are each independently at least one monovalent anion, and n is a real number satisfying $0 \leq n \leq 3$, and

40 <Formula 2> $[A^2][B^2][X^2_{(3-m)}Y^2_m]$

wherein, in Formula 2,

45 A^2 is at least one monovalent organic cation, at least one monovalent inorganic cation, or any combination thereof, B^2 is at least one divalent inorganic cation, X^2 and Y^2 are each independently at least one monovalent anion, and m is a real number satisfying $0 \leq m \leq 3$.

50 **[0007]** According to an aspect of another example embodiment, a method of manufacturing a photoelectric conversion device includes: forming a first conductive layer; forming an electron blocking layer including the first perovskite compound represented by Formula 1 on the first conductive layer; forming a photoelectric conversion layer on the electron blocking layer; forming a hole blocking layer including the second perovskite compound represented by Formula 2 on the photoelectric conversion layer; and forming a second conductive layer on the hole blocking layer.

55 **[0008]** According to an aspect of another example embodiment, an imaging device includes a light irradiation unit, a photodetector unit, and a control unit, the photodetector unit including the above-described photoelectric conversion device.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] These and/or other aspects will become apparent and more readily appreciated from the following description of the example embodiments, taken in conjunction with the accompanying drawings in which:

FIG. 1 is a schematic cross-sectional side view of a photoelectric conversion device according to an embodiment;
 FIGS. 2A and 2B are schematic illustrations of energy levels of a photoactive material in a photoelectric conversion layer, and a first perovskite compound in an electron blocking layer;
 FIGS. 3A and 3B are schematic illustrations of energy levels of a photoactive material in a photoelectric conversion layer, and a second perovskite compound in a hole blocking layer;
 FIG. 4 is a schematic view for describing a method of operating a photoelectric conversion device according to another embodiment;
 FIGS. 5A to 5E are schematic cross-sectional views for describing a method of manufacturing a photoelectric conversion device according to an embodiment;
 FIGS. 6A to 6C are surface images of an electron blocking layer, a photoelectric conversion layer, and a hole blocking layer in a photoelectric conversion device of Example 1, respectively;
 FIG. 7 is a graph of current density with respect to voltage, illustrating the experimental results of Evaluation Example 1 for photoelectric conversion devices of Examples 1 to 3 and Comparative Examples 1 and 2;
 FIG. 8 is a graph of current density with respect to voltage, illustrating the experimental results of Evaluation Example 2 for photoelectric conversion devices of Comparative Examples 3 and 4;
 FIG. 9 is a graph of photoelectric current with respect to time, illustrating the experimental results of Evaluation Example 3 for the photoelectric conversion device of Example 2;
 FIGS. 10A and 10B are graphs showing photoabsorption and photoluminescent characteristics of photoelectric conversion devices of Comparative Examples 1 and 5, as a result of Evaluation Example 4;
 FIG. 11 is a scanning electron microscope (SEM) image of the electron blocking layer in the photoelectric conversion device of Example 1;
 FIGS. 12A to 12C are scanning electron microscope (SEM) images of the photoelectric conversion layer in the photoelectric conversion device of Example 1, wherein FIGS. 12B and 12C are magnified images of FIGS. 12A and 12B, respectively, and a scale bar length is 400 μm ;
 FIG. 13 is a SEM image of the hole blocking layer in the photoelectric conversion device of Example 1; and
 FIGS. 14A and 14B are SEM images of a hole blocking layer in the photoelectric conversion device of Example 2, wherein FIG. 14B is a magnified image of FIG. 14A.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0010] Reference will now be made in detail to example embodiments of a photoelectric conversion device, a method of operating the photoelectric conversion device, and a method of manufacturing the photoelectric conversion device, examples of which are illustrated in the accompanying drawings, wherein like reference numerals refer to like elements throughout. In this regard, the present example embodiments may have different forms and should not be construed as being limited to the descriptions set forth herein. Accordingly, the example embodiments are merely described below, by referring to the figures, to explain aspects. In the drawings, like reference numerals denote like elements throughout, and thus redundant description thereof will be omitted. In the drawings, the sizes of elements are exaggerated or reduced for ease of description. As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items. Expressions such as "at least one of," when preceding a list of elements, modify the entire list of elements and do not modify the individual elements of the list.

[0011] It will also be understood that when an element such as a layer, a region, or a component is referred to as being "on" another element, it can be "directly on" the other element, or intervening layers, regions, or components may also be present.

[0012] Although the terms "first", "second", etc., may be used herein to describe various elements, components, regions, and/or layers, these elements, components, regions, and/or layers should not be limited by these terms. These terms are used only to distinguish one component from another, not for purposes of limitation.

[0013] General and widely used terms have been employed herein, in consideration of functions provided in the present disclosure, and may vary according to an intention of one of ordinary skill in the art, a precedent, or emergence of new technologies. Additionally, in some cases, an applicant may arbitrarily select specific terms. Then, the applicant will provide the meaning of the terms in the description of the present disclosure. Accordingly, it will be understood that the terms used herein should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein. As used herein, the term "perovskite compound" refers to a compound represented by, for example, the formula of ABX_3 ,

wherein A and B are cations having different sizes, and X is an anion. In the unit cell of the perovskite compound, a site of the cation A may be at (0,0,0), a site of the cation B may be at (1/2,1/2,1/2), and a site of the anion X may be at (1/2,1/2,0). The perovskite compound may have a twisted structure with lower symmetry, compared to the ideal symmetric structure of calcium titanium oxide (CaTiO₃), depending on types of A, B, and X. It will be understood that the perovskite compound used herein may encompass a compound having the ideal symmetric structure and a compound having a twisted structure with low symmetry.

[0014] FIG. 1 is a schematic cross-sectional side view of a photoelectric conversion device 100 according to an embodiment.

[0015] Referring to FIG. 1, the photoelectric conversion device 100 may include a first conductive layer 110, a second conductive layer 150, an electron blocking layer 120, a photoelectric conversion layer 130, and a hole blocking layer 140.

[0016] The electron blocking layer 120, the photoelectric conversion layer 130 and the hole blocking layer 140 may be between the first conductive layer 110 and the second conductive layer 150.

[0017] The electron blocking layer 120 may be between the first conductive layer 110 and the photoelectric conversion layer 130.

[0018] The hole blocking layer 140 may be between the second conductive layer 150 and the photoelectric conversion layer 130.

[0019] The electron blocking layer 120 may include a first perovskite compound represented by Formula 1.



[0020] In Formula 1, A¹ may be at least one monovalent organic cation, at least one monovalent inorganic cation, or any combination thereof.

[0021] For example, in Formula 1, A¹ may be i) a monovalent organic cation, ii) a monovalent inorganic cation, iii) at least two different monovalent organic cations, iv) at least two different monovalent inorganic cations, or v) any combination of at least one monovalent organic cation and at least one monovalent inorganic cation. However, example embodiments are not limited thereto.

[0022] In some example embodiments, in Formula 1, A¹ may be (R₁R₂R₃C)⁺, (R₁R₂R₃R₄N)⁺, (R₁R₂R₃R₄P)⁺, (R₁R₂R₃R₄As)⁺, (R₁R₂R₃R₄Sb)⁺, (R₁R₂N=C(R₃)-NR₄R₅)⁺, a substituted or unsubstituted nitrogen-containing 5-membered cyclic monovalent cation, a substituted or unsubstituted nitrogen-containing 6-membered cyclic monovalent cation, a substituted or unsubstituted 7-membered cyclic monovalent cation, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Fr⁺, or any combination thereof;

R₁ to R₅, at least one substituent of the substituted nitrogen-containing 5-membered cyclic monovalent cation, at least one substituent of the substituted nitrogen-containing 6-membered cyclic monovalent cation, and at least one substituent of the substituted 7-membered cyclic monovalent cation may be each independently selected from hydrogen, deuterium (-D), -F, -Cl, -Br, -I, a hydroxyl group, a substituted or unsubstituted C₁-C₁₀ alkyl group, a substituted or unsubstituted C₂-C₁₀ alkenyl group, a substituted or unsubstituted C₂-C₁₀ alkynyl group, a substituted or unsubstituted C₁-C₁₀ alkoxy group, a substituted or unsubstituted C₆-C₂₀ aryl group, and -N(Q₁)(Q₂); and

Q₁ and Q₂ may be each independently selected from hydrogen, deuterium, a hydroxyl group, a C₁-C₂₀ alkyl group, a C₂-C₂₀ alkenyl group, a C₂-C₂₀ alkynyl group, a C₁-C₂₀ alkoxy group, and a C₆-C₂₀ aryl group. However, example embodiments are not limited thereto.

[0023] In some other example embodiments, in Formula 1, A¹ may be (R₁R₂R₃C)⁺, (R₁R₂R₃R₄N)⁺, (R₁R₂R₃R₄P)⁺, (R₁R₂R₃R₄As)⁺, (R₁R₂R₃R₄Sb)⁺, (R₁R₂N=C(R₃)-NR₄R₅)⁺, a substituted or unsubstituted cycloheptatrienium, a substituted or unsubstituted imidazolium, a substituted or unsubstituted pyridinium, a substituted or unsubstituted pyridazinium, a substituted or unsubstituted pyrimidinium, a substituted or unsubstituted pyrazinium, a substituted or unsubstituted pyrazolium, a substituted or unsubstituted thiazolium, a substituted or unsubstituted oxazolium, a substituted or unsubstituted piperidinium, a substituted or unsubstituted pyrrolidinium, a substituted or unsubstituted pyrrolinium, a substituted or unsubstituted pyrrolium, a substituted or unsubstituted triazolium, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Fr⁺, or any combination thereof;

R₁ to R₅, at least one substituent of the substituted cycloheptatrienium, at least one substituent of the substituted imidazolium, at least one substituent of the substituted pyridinium, at least one substituent of the substituted pyridazinium, at least one substituent of the substituted pyrimidinium, at least one substituent of the substituted pyrazinium, at least one substituent of the substituted pyrazolium, at least one substituent of the substituted thiazolium, at least one substituent of the substituted oxazolium, at least one substituent of the substituted piperidinium, at least one substituent of the substituted pyrrolidinium, at least one substituent of the substituted pyrrolinium, at least one substituent of the substituted pyrrolium, and at least one substituent of the substituted triazolium may be each independently selected from hydrogen, deuterium, -F, -Cl, -Br, -I, a hydroxyl group, a C₁-C₂₀ alkyl group, a C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl group, and a C₁-C₂₀ alkoxy group;

a C₁-C₂₀ alkyl group, a C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl group, and a C₁-C₂₀ alkoxy group, each substituted with

at least one selected from deuterium, -F, -Cl, -Br, -I, and a hydroxyl group;
 a phenyl group, a naphthyl group, a biphenyl group, and a terphenyl group,
 a phenyl group, a naphthyl group, a biphenyl group, and a terphenyl group, each substituted with at least one selected
 from deuterium, -F, -Cl, -Br, -I, a hydroxyl group, a C₁-C₂₀ alkyl group, a C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl group,
 and a C₁-C₂₀ alkoxy group, and
 -N(Q₁)(Q₂); and

Q₁ and Q₂ may each independently be selected from hydrogen, deuterium, a C₁-C₂₀ alkyl group, a C₂-C₁₀ alkenyl group,
 a C₂-C₁₀ alkynyl group, a C₁-C₂₀ alkoxy group, a phenyl group, a naphthyl group, a biphenyl group, and a terphenyl
 group. However, example embodiments are not limited thereto.

[0024] In some other example embodiments, in Formula 1, A¹ may be (R₁R₂R₃R₄N)⁺, (R₁R₂R₃R₄P)⁺, (R₁R₂R₃R₄As)⁺,
 (R₁R₂R₃R₄Sb)⁺, (R₁R₂N=C(R₃)-NR₄R₅)⁺, a substituted or unsubstituted cycloheptatrienium, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Fr⁺,
 or any combination thereof;

R₁ to R₅, and at least one substituent of the substituted cycloheptatrienium may each independently be selected from
 hydrogen, deuterium, -F, -Cl, -Br, -I, a hydroxyl group, a C₁-C₂₀ alkyl group, a C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl
 group, a C₁-C₂₀ alkoxy group, and -N(Q₁)(Q₂); and

Q₁ and Q₂ may each independently be selected from hydrogen, deuterium, a C₁-C₂₀ alkyl group, a C₂-C₁₀ alkenyl group,
 a C₂-C₁₀ alkynyl group, and a C₁-C₂₀ alkoxy group. However, example embodiments are not limited thereto.

[0025] In some example embodiments, in Formula 1, A¹ may be (CH₃NH₃)⁺, ((CH₃)₂PH₂)⁺, (CH₃AsH₃)⁺, (NH₄)⁺,
 (CH₃SbH₃)⁺, (PH₄)⁺, (PF₄)⁺, (CH₃PH₃)⁺, (C₇H₇)⁺, (SbH₄)⁺, (ASH₄)⁺, (NCl₄)⁺, (NH₃OH)⁺, (NH₃NH₂)⁺, (CH(NH₂)₂)⁺,
 (C₃N₂H₅)⁺, ((CH₃)₂NH₂)⁺, (NC₄H₉)⁺, ((CH₃CH₂)NH₃)⁺, ((NH₂)₃C)⁺, ((CH₃CH₂CH₂CH₂)NH₃)⁺, (NH₂CHNH₂)⁺, Li⁺, Na⁺,
 K⁺, Rb⁺, Cs⁺, Fr⁺, or any combination thereof. However, example embodiments are not limited thereto.

[0026] In some example embodiments, in Formula 1, A¹ may be (CH₃NH₃)⁺, ((CH₃CH₂CH₂CH₂)NH₃)⁺, (NH₂CHNH₂)⁺,
 K⁺, Rb⁺, Cs⁺, or any combination thereof. However, example embodiments are not limited thereto.

[0027] In Formula 1, B¹ may be at least one divalent inorganic cation.

[0028] For example, in Formula 1, B¹ may be i) a divalent inorganic cation, or ii) a combination of at least two different
 divalent inorganic cations. However, example embodiments are not limited thereto.

[0029] In some example embodiments, in Formula 1, B¹ may be a divalent cation of a rare earth metal, a divalent
 cation of an alkali earth metal, a divalent cation of a transition metal, a divalent cation of a late transition metal, or any
 combination thereof. However, example embodiments are not limited thereto.

[0030] In some other example embodiments, in Formula 1, B¹ may be La²⁺, Ce²⁺, Pr²⁺, Nd²⁺, Pm²⁺, Sm²⁺, Eu²⁺,
 Gd²⁺, Tb²⁺, Dy²⁺, Ho²⁺, Er²⁺, Tm²⁺, Yb²⁺, Lu²⁺, Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Ra²⁺, Pb²⁺, Sn²⁺, or any combination
 thereof. However, example embodiments are not limited thereto.

[0031] In some other example embodiments, in Formula 1, B¹ may be Pb²⁺, Sn²⁺, or any combination thereof. However,
 example embodiments are not limited thereto.

[0032] In some other example embodiments, in Formula 1, B¹ may be Pb²⁺. However, example embodiments are not
 limited thereto.

[0033] For example, in Formula 1, X¹ and Y¹ may each independently be at least one monovalent anion, wherein X¹
 and Y¹ may be the same as or different from each other.

[0034] For example, in Formula 1, X¹ and Y¹ may each independently be i) a monovalent anion, or ii) any combination
 of at least two different monovalent anions. However, example embodiments are not limited thereto.

[0035] In some example embodiments, in Formula 1, X¹ and Y¹ may each independently be at least one halide anion.
 However, example embodiments are not limited thereto.

[0036] In some example embodiments, in Formula 1, X¹ and Y¹ may each independently be selected from Cl⁻, Br⁻,
 and I⁻. However, example embodiments are not limited thereto.

[0037] In Formula 1, n may be a real number satisfying 0 ≤ n ≤ 3.

[0038] For example, in Formula 1, n may be a real number satisfying 0 ≤ n < 3. However, example embodiments are
 not limited thereto.

[0039] The hole blocking layer 140 may include second a perovskite compound represented by Formula 2.



[0040] In Formula 2, A² may be defined substantially the same as A¹ in Formula 1 as described above, B² may be
 defined substantially the same as B¹ in Formula 1 as described above, X² may be defined substantially the same as X¹
 in Formula 1 as described above, Y² may be defined substantially the same as Y¹ in Formula 1 as described above,
 and m may be defined substantially the same as n in Formula 1 as described above.

[0041] In some example embodiments, the first perovskite compound represented by Formula 1 and the second
 perovskite compound represented by Formula 2 may each independently be selected from CH₃NH₃PbI₃, CH₃NH₃PbBr₃,
 CH₃NH₃PbBr₍₃₋₀₎I₀, CH₃NH₃PbCl₍₃₋₀₎Br₀, CH₃NH₃PbCl₍₃₋₀₎I₀, CsPbI₃, CsPbBr₃, CH₃CH₂CH₂CH₂NH₃PbBr₃,

$\text{NH}_2\text{CHNH}_2\text{PbBr}_3$, $\text{NH}_2\text{CHNH}_2\text{PbBr}_{(3-o)}\text{I}$, $[\text{CH}_3\text{NH}_3]_{(1-x)}[\text{NH}_2\text{CHNH}_2]_x\text{PbBr}_3$, and $[\text{CH}_3\text{NH}_3]_{(1-x)}[\text{NH}_2\text{CHNH}_2]_x\text{PbBr}_{(3-o)}\text{I}$, wherein o may be a real number greater than 0 and less than 3, and x may be a real number greater than 0 and less than 1. However, example embodiments are not limited thereto.

[0042] The electron blocking layer 120 may further include a polymer together with the first perovskite compound represented by Formula 1.

[0043] The hole blocking layer 140 may further include a polymer together with the second perovskite compound represented by Formula 2.

[0044] The polymer may be soluble and miscible with the first perovskite compound or the second perovskite compound in a solvent. For example, the polymer may be a polar polymer soluble and miscible in a polar solvent.

[0045] An amount of the polar polymer in the electron blocking layer 120 may be about 5 parts to about 60 parts by weight, and in some embodiments, about 10 parts to about 50 parts by weight, and in some other embodiments, about 20 parts to about 40 parts by weight, with respect to 100 parts by weight of the first perovskite compound represented by Formula 1. When the amount of the polar polymer in the electron blocking layer 120 is within these ranges, the electron blocking layer 120 may have improved electron blocking ability due to improved adhesion to the photoelectric conversion layer 130. Accordingly, the electron blocking layer 120 may increase photoelectric conversion efficiency by reducing dark current.

[0046] An amount of the polar polymer in the hole blocking layer 140 may be about 5 parts to about 60 parts by weight, and in some embodiments, about 10 parts to about 50 parts by weight, and in some other embodiments, about 20 parts to about 40 parts by weight, with respect to 100 parts by weight of the second perovskite compound represented by Formula 2. When the amount of the polar polymer in the hole blocking layer 140 is within these ranges, the hole blocking layer 140 may have improved hole blocking ability due to improved adhesion to the photoelectric conversion layer 130. Accordingly, the hole blocking layer 140 may increase photoelectric conversion efficiency by reducing dark current.

[0047] For example, the polar polymer may be polyamic acid, polyimide, polyvinyl alcohol (PVA), polyacrylic acid, polyhydroxyethyl methacrylate (PHEMA), polymethyl methacrylate (PMMA), polyacrylate, or polyacrylonitrile (PAN). However, example embodiments are not limited thereto. The polymer may include a copolymer of the above-listed polymer materials.

[0048] The polymer may further improve adhesion of the electron blocking layer 120 or the hole blocking layer 140 by being mixed with the first perovskite compound or the second perovskite compound, further improving electron blocking ability or hole blocking ability and consequentially leading to reduced dark current and improved photoelectric conversion efficiency. For example, the polymer may form a complex with a perovskite compound in the electron blocking layer 120 or the hole blocking layer 140. For example, in the electron blocking layer 120 or the hole blocking layer 140, the polymer may be in a separate phase from the perovskite phase and thus form separate double layers.

[0049] The solvent may include any of various solvents. For example, the solvent may include water, methanol, ethanol, acetone, benzene, toluene, hexane, acetonitrile, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), γ -butyrolactone, N-methylpyrrolidone (NMP), methylene chloride (CH_2Cl_2), chloroform (CH_3Cl), tetrahydrofuran (THF), or any mixture thereof.

[0050] In some example embodiments, the electron blocking layer 120 may further include polyimide as a polar polymer together with $\text{CH}_3\text{NH}_3\text{PbI}_3$. However, example embodiments are not limited thereto. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ may be polycrystalline. However, example embodiments are not limited thereto. For example, the electron blocking layer 120 may include a $\text{CH}_3\text{NH}_3\text{PbI}_3$ -polyimide complex. However, example embodiments are not limited thereto. For example, the electron blocking layer 120 may include two separate $\text{CH}_3\text{NH}_3\text{PbI}_3$ and polyimide layers. However, example embodiments are not limited thereto.

[0051] In some example embodiments, the hole blocking layer 140 may further include polyimide as a polar polymer together with $\text{CH}_3\text{NH}_3\text{PbBr}_3$. However, example embodiments are not limited thereto. The $\text{CH}_3\text{NH}_3\text{PbBr}_3$ may be polycrystalline. However, example embodiments are not limited thereto. For example, the hole blocking layer 140 may include a $\text{CH}_3\text{NH}_3\text{PbBr}_3$ -polyimide complex. However, example embodiments are not limited thereto. For example, the hole blocking layer 140 may include two separate $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and polyimide layers. However, example embodiments are not limited thereto.

[0052] In some example embodiments, a surface of the hole blocking layer 140 may have various regular or irregular patterns, including, for example, a square star pattern, a butterfly pattern, a starfish pattern, a sawtooth pattern, and a clover pattern. However, example embodiments are not limited thereto.

[0053] The electron blocking layer 120 may have a thickness of about 1 nm to about 10 μm . For example, the electron blocking layer 120 may have a thickness of about 10 nm to about 10 μm , and in some example embodiments, about 50 nm to about 5000 nm. However, example embodiments are not limited thereto. When the thickness of the electron blocking layer 120 is within these ranges, the photoelectric conversion device may have a satisfactory dark current reduction effect and a photoelectric conversion efficiency that is maintained at a similar level without significant reduction.

[0054] The electron blocking layer 120 may be formed as described below.

[0055] The hole blocking layer 140 may have a thickness of about 1 nm to about 10 μm . For example, the hole blocking

layer 140 may have a thickness of about 10 nm to about 10 μm , and in some example embodiments, about 50 nm to about 5000 nm. However, example embodiments are not limited thereto. When the thickness of the hole blocking layer 140 is within these ranges, the photoelectric conversion device may have a satisfactory dark current reduction effect and a photoelectric conversion efficiency that is maintained at a similar level without significant reduction.

[0056] The hole blocking layer 140 may be formed as described below.

[0057] The photoelectric conversion layer 130 may include a semiconductor material as a photoactive material, for example, amorphous Se, CdZnTe, GaAs, InP, Si, or any combination thereof. However, example embodiments are not limited thereto.

[0058] In some example embodiments, the photoelectric conversion layer 130 may include a third perovskite compound represented by Formula 3, which will be described later, as the photoactive material. However, example embodiments are not limited thereto.

[0059] A method of forming the photoelectric conversion layer 130 is not specifically limited, and any of a variety of methods, including a solution process such as doctor blade coating or deposition may be used.

[0060] FIGS. 2A and 2B are schematic illustrations of energy levels of the photoactive material included in the photoelectric conversion layer 130, and the first perovskite compound included in the electron blocking layer 120.

[0061] Referring to FIGS. 2A and 2B, the lowest unoccupied molecular orbital (LUMO) energy level (E_{C_L}) of the photoactive material may be equal to or lower than the LUMO energy level (E_{C_P1}) of the first perovskite compound. Generally, when an external voltage is applied to a photoelectric conversion device, injection of holes and electrons may occur, leading to an increased dark current. However, when the condition of $E_{C_L} \leq E_{C_P1}$ is satisfied, electron transfer may be blocked, and a dark current reduction effect may be obtained.

[0062] Referring to FIG. 2A, the highest occupied molecular orbital (HOMO) energy level (E_{V_L}) of the photoactive material may be equal to or lower than the HOMO energy level (E_{V_P1}) of the first perovskite compound. However, example embodiments are not limited thereto. Referring to FIG. 2B, the HOMO energy level (E_{V_L}) of the photoactive material may be greater than the HOMO energy level (E_{V_P1}) of the first perovskite compound. However, example embodiments are not limited thereto.

[0063] FIGS. 3A and 3B are schematic illustrations of energy levels of the photoactive material included in the photoelectric conversion layer 130, and the second perovskite compound included in the hole blocking layer 140.

[0064] Referring to FIGS. 3A and 3B, the HOMO energy level (E_{V_L}) of the photoactive material may be greater than or equal to the HOMO energy level (E_{V_P2}) of the second perovskite compound. When an external voltage is applied to a photoelectric conversion device, injection of holes and electrons may occur, leading to an increased dark current. However, when the condition of $E_{V_L} \geq E_{V_P2}$ is satisfied, hole transfer may be blocked, and a dark current reduction effect may be obtained.

[0065] Referring to FIG. 3A, the LUMO energy level (E_{C_L}) of the photoactive material may be greater than or equal to the LUMO energy level (E_{C_P2}) of the second perovskite compound. However, example embodiments are not limited thereto. Referring to FIG. 3B, the LUMO energy level (E_{C_L}) of the photoactive material may be lower than the LUMO energy level (E_{C_P2}) of the second perovskite compound. However, example embodiments are not limited thereto.

[0066] The photoelectric conversion layer 130 may include a third perovskite compound represented by Formula 3.



[0067] In Formula 3 ,

A^3 may be at least one monovalent organic cation, at least one monovalent inorganic cation, or any combination thereof,

B^3 may be at least one divalent inorganic cation,

X^3 and Y^3 may each independently be at least one monovalent anion, and

k may be a real number satisfying $0 \leq k \leq 3$.

[0068] The third perovskite compound may be polycrystalline. The term "polycrystalline" used herein may refer to a form in which crystals are bound to one another. That is, the third perovskite compound may have a structure in which crystals are fused to each other. However, example embodiments are not limited thereto. The photoelectric conversion layer 130 may have a cross-sectional form as illustrated in FIG. 12A. However, example embodiments are not limited thereto. When the third perovskite compound is polycrystalline, effects of a dark current reduction and a photoelectric conversion efficiency increase may be obtained.

[0069] The longest axis of a crystal in the third perovskite compound may be about 1 μm to about 300 μm , and in some example embodiments, about 10 μm to about 50 μm . However, example embodiments are not limited thereto. When the longest axis of a crystal in the third perovskite compound is within these ranges, a photoelectric conversion device with a sufficient dark current reduction effect may be obtained without reduction in photoelectric conversion

efficiency.

[0070] In Formula 3, A^3 may be defined substantially the same as A^1 in Formula 1 as described above, B^3 may be defined substantially the same as B^1 in Formula 1 as described above, X^3 may be defined substantially the same as X^1 in Formula 1 as described above, Y^3 may be defined substantially the same as Y^1 in Formula 1 as described above, and k may be defined substantially the same as n in Formula 1 as described above.

[0071] In some example embodiments, the third perovskite compound represented by Formula 3 may be $CH_3NH_3PbI_3$. However, example embodiments are not limited thereto.

[0072] The photoelectric conversion layer 130 may absorb light, for example, infrared rays, visible rays, or X-rays. In some example embodiments, the photoelectric conversion layer 130 may absorb X-rays.

[0073] In a solar cell, an infrared imaging device and a visible light imaging device, generally a photoelectric conversion layer using a perovskite compound may be formed by deposition such as spin coating to have a thickness of about 1 μm or less. However, in an X-ray imaging device, it may be difficult to form a perovskite photoelectric conversion layer having a thickness of hundreds of micrometers over a wide region by deposition.

[0074] To address this drawback, solution process-based doctor blade coating may be used to form a polycrystalline perovskite photoelectric conversion layer having a thickness of hundreds of micrometers.

[0075] In some example embodiments, the photoelectric conversion layer 130 may have a thickness of about 0.1 μm to about 1,500 μm . When the thickness of the photoelectric conversion layer 130 is within this range, photoelectric conversion efficiencies of infrared rays, visible rays, and even light having a short wavelength, such as X-rays, may be improved.

[0076] However, example embodiments are not limited thereto. In some example embodiments, when the light is provided as visible rays or infrared rays, the photoelectric conversion layer 130 may have a thickness of about 0.1 μm to about 1 μm . However, example embodiments are not limited thereto.

[0077] However, example embodiments are not limited thereto. In some other example embodiments, when the light is provided as X-rays, the photoelectric conversion layer 130 may have a thickness of about 300 μm to about 1,500 μm .

However, example embodiments are not limited thereto.

[0078] In some example embodiments, the first conductive layer 110 and the second conductive layer 150 may be reflective, transmissive, or semi-transmissive depending on a use.

[0079] The first conductive layer 110 and the second conductive layer 150 may include a conductive material(s), for example, a metal, a metal oxide, an electrically conductive organic compound, or a combination thereof. For example, when the first conductive layer 110 is transmissive, a material for forming the first conductive layer 110 may be selected from indium tin oxide (ITO), indium zinc oxide (IZO), tin oxide (SnO_2), zinc oxide (ZnO), and any combination thereof. However, example embodiments are not limited thereto. For example, when the first conductive layer 110 is semi-transmissive or reflective, the material for forming the first conductive layer 110 may be selected from gold (Au), silver (Ag), chromium (Cr), nickel (Ni), and any combination thereof. However, example embodiments are not limited thereto. The above-listed materials for forming the first conductive layer 110 may be used as materials for forming the second conductive layer 150, and thus a detailed description of the second conductive layer 150 will be omitted here.

[0080] In some example embodiments, when the light is provided as X-rays, the second conductive layer 150 may be reflective, transmissive, or semi-transmissive.

[0081] In some other example embodiments, when the light is provided as infrared rays or visible rays, the second conductive layer 150 may be transmissive. The second conductive layer 150 may be transmissive enough to allow light to enter the photoelectric conversion device through the second conductive layer 150.

[0082] The first conductive layer 110 and the second conductive layer 150 may have any thickness not specifically limited, for example, a thickness of about 10 nm to about 2,000 nm. However, example embodiments are not limited thereto.

[0083] Methods of forming the first conductive layer 110 and the second conductive layer 150 are not specifically limited, and may include a variety of methods, including coating, deposition, and the like.

[0084] FIG. 4 is a schematic view for describing a method of operating a photoelectric conversion device according to an embodiment in a flat type imaging device. However, example embodiments are not limited thereto.

[0085] Referring to FIG. 4, a photoelectric conversion device according to an embodiment may include: first conductive layers 411, 412, and 413; a second conductive layer 450; and an electron blocking layer 420, a photoelectric conversion layer 430 and a hole blocking layer 440 which are between the first conductive layers 411, 412, and 413 and the second conductive layer 450.

[0086] The electron blocking layer 420 may be between the first conductive layers 411, 412, and 413 and the photoelectric conversion layer 430. The hole blocking layer 440 may be between the second conductive layer 450 and the photoelectric conversion layer 430.

[0087] The electron blocking layer 420 may include a first perovskite compound represented by Formula 1. The hole blocking layer 440 may include a second perovskite compound represented by Formula 2.

[0088] An electric field may be applied to the first conductive layers 411, 412, and 413, which serve as a negative

electrode (negative bias), and the second conductive layer 450, which serves as a positive electrode (positive bias).

[0089] Unless stated otherwise, the above-described descriptions of the first conductive layer 110, the second conductive layer 150, the electron blocking layer 120, the photoelectric conversion layer 130, and the hole blocking layer 140 apply respectively to the first conductive layers 411, 412, and 413, the second conductive layer 450, the electron blocking layer 120, the photoelectric conversion layer 430, and the hole blocking layer 440, and thus detailed descriptions thereof will not be provided.

[0090] The second conductive layer 450 may be connected to a power source 470, so that an electric field may be applied to the second conductive layer 450. The opposite terminal of the power source 470 may be grounded. Accordingly, an electric field may be produced between the first conductive layers 411, 412, and 413 and the second conductive layer 450. When light 480 is incident onto the photoelectric conversion layer 430, the light 480 is converted into electrons and holes by the photoactive material of the photoelectric conversion layer 430. The electrons and holes are moved to the second conductive layer 450 and the first conductive layers 411, 412, and 413, respectively, by the electric field.

[0091] The first conductive layers 411, 412, and 413 may be connected to detectors 461, 462, and 463, respectively. The first conductive layers 411, 412, and 413 may be between the detectors 461, 462, and 463 and the electron blocking layer 420. That is, the detectors 461, 462, and 463 may be arranged on a bottom surface (i.e., a light exit surface) of the photoelectric conversion layer 430.

[0092] The detectors 461, 462, and 463 may detect charges 490 generated in the photoelectric conversion layer 430. The detectors 461, 462, and 463 may include storage capacitors 461a, 462a, and 463a and readout circuits 461b, 462b, and 463b, respectively. The readout circuits 461b, 462b, and 463b may read out the charges 490 collected by the storage capacitors 461a, 462a, and 463a, respectively.

[0093] The readout circuits 461b, 462b, and 463b may respectively convert the amounts of charges in the storage capacitors 461a, 462a, and 463a into digital signals. The digital signals may be converted into image signals by a signal processing unit (not shown).

[0094] The second conductive layer 450, the electron blocking layer 420, the photoelectric conversion layer 430, and the hole blocking layer 440 may be formed to cover the first conductive layers 411, 412, and 413.

[0095] FIGS. 5A to 5E are schematic cross-sectional views for describing a method of manufacturing a photoelectric conversion device according to an embodiment.

[0096] A method of manufacturing a photoelectric conversion device according to an embodiment may include: providing a first conductive layer; providing a first mixture including a A¹-containing precursor, a B¹-containing precursor, and a solvent to form an electron blocking layer including a first perovskite compound represented by Formula 1; forming a photoelectric conversion layer on the electron blocking layer; providing a second mixture including a A²-containing precursor, a B²-containing precursor, and a solvent to form a hole blocking layer including a second perovskite compound represented by Formula 2; and providing a second conductive layer on the hole blocking layer.

[0097] First, as illustrated in FIG. 5A, a first conductive layer 510 may be provided. The first conductive layer 510 may be the same as the first conductive layer 110 described above with reference to FIG. 1. The first conductive layer 510 may be provided using any of a variety of methods known in the art, and thus, a detailed description thereof will be omitted here.

[0098] Next, an electron blocking layer 520 may be provided on the first conductive layer 510. The electron blocking layer 520 may include a first perovskite compound represented by Formula 1. The first perovskite compound represented by Formula 1 may be obtained from a first mixture including an A¹-containing precursor, a B¹-containing precursor, and a solvent.

[0099] The electron blocking layer 520 may further include a polymer, together with the first perovskite compound. In this regard, the first mixture may further include the polymer or a precursor thereof.

[0100] The polymer may be any of a variety of polymers. The polymer may be a polar polymer that may be soluble and miscible with the first perovskite compound in a solvent. For example, the polar polymer may be polyamic acid, polyimide, polyvinyl alcohol (PVA), polyacrylic acid, polyhydroxyethyl methacrylate (PHEMA), polymethyl methacrylate (PMMA), polyacrylate, or polyacrylonitrile (PAN). However, example embodiments are not limited thereto. The polymer may include a copolymer of the above-listed polymer materials.

[0101] For example, the first mixture may be spin-coated on the first conductive layer 510. When the first mixture is applied onto the first conductive layer 510 by spin coating, appropriate spin coating conditions may be chosen from, for example, a coating rate range of about 2,000 rpm to about 4,000 rpm and a temperature range of about 80°C to about 200°C, in consideration of the composition of the first mixture and the structure of the electron blocking layer 520.

[0102] The first mixture may be applied onto the first conductive layer 510 by using any of a variety of methods known in the art.

[0103] The first mixture applied onto the first conductive layer 510 may be thermally treated to form the electron blocking layer 520. The thermal treatment temperature may be in a range of about 100°C to about 300°C. When the thermal treatment temperature is less than 100°C, the electron blocking layer 520 may have reduced adhesion. When the thermal treatment temperature exceeds 300°C, the first perovskite compound may be damaged.

[0104] For example, appropriate thermal treatment conditions may be chosen from a temperature range of about 100°C to about 300°C for about 15 minutes to about 2 hours in consideration of the composition of the first mixture and the structure of the electron blocking layer 520.

[0105] The electron blocking layer 520 formed as described above may include the first perovskite compound. For example, the electron blocking layer 520 may include the first perovskite compound and the polar polymer, and in some embodiments, a composite of the first perovskite compound and the polar polymer, and in some other embodiments, two separate layers including the first perovskite compound and the polar polymer, respectively.

[0106] In the A¹-containing precursor and the B¹-containing precursor, A¹ and B¹ may be defined the same as described above in connection with Formula 1.

[0107] For example, the A¹-containing precursor may be selected from halides of A¹ (for example, (A¹)(X¹)), and the B¹-containing precursor may be selected from halides of B¹ (for example, (B¹)(Y¹)₂). In the (A¹)(X¹) and (B¹)(Y¹)₂, A¹, B¹, X¹, and Y¹ may be defined the same as described above in connection with Formula 1.

[0108] The solvent may be selected from the materials in which the A¹-containing precursor and the B¹-containing precursor have high solubility. For example, the solvent may be dimethylformamide, dimethyl sulfoxide, γ -butyrolactone, N-methyl-2-pyrrolidone, or any combination thereof. However, example embodiments are not limited thereto.

[0109] Next, a photoelectric conversion layer 530 may be provided onto the electron blocking layer 520. The photoelectric conversion layer 530 may include a third perovskite compound represented by Formula 3. The third perovskite compound represented by Formula 3 may be obtained from a third mixture prepared by adding a non-solvent to a mixture including an A³-containing precursor, a B³-containing precursor, and a solvent and then stirring at a temperature of about 70°C to about 120°C.

[0110] The solvent may be selected from the materials in which the A³-containing precursor and the B³-containing precursor have high solubility. For example, the solvent may be dimethylformamide, dimethyl sulfoxide, γ -butyrolactone, or any combination thereof. However, example embodiments are not limited thereto.

[0111] The non-solvent may be selected from the materials in which the A³-containing precursor and the B³-containing precursor have low solubility. For example, the non-solvent may be α -terpineol, hexyl carbitol, butyl carbitol acetate, hexyl cellosolve, or butyl cellosolve acetate. However, example embodiments are not limited thereto.

[0112] For example, the third mixture may be coated on the electron blocking layer 520 by doctor blade coating or bar coating. The third mixture may have increased viscosity due to the addition of the non-solvent, and thus may be applied by doctor blade coating or bar coating. When the third mixture is applied onto the electron blocking layer 520 by doctor blade coating, appropriate doctor blade coating conditions may be chosen within a temperature range of about 80°C to about 200°C in consideration of the composition of the third mixture and the structure of the photoelectric conversion layer 530.

[0113] The third mixture may be applied onto the electron blocking layer 520 by using any of a variety of methods known in the art.

[0114] The third mixture applied onto the electron blocking layer 520 may be thermally treated to form the photoelectric conversion layer 530.

[0115] For example, appropriate thermal treatment conditions may be chosen from a temperature range of about 100°C to about 200°C for about 15 minutes to about 2 hours in consideration of the composition of the third mixture and the structure of the photoelectric conversion layer 530.

[0116] Optionally, after the third mixture is applied onto the electron blocking layer 520 to form a preliminary photoelectric conversion layer including the third perovskite compound represented by Formula 3, the preliminary photoelectric conversion layer may be pressed at a high temperature (for example, in a temperature range of about 100°C to about 200°C) under high pressure (for example, in a pressure range of about 5 atm to about 10 atm) to obtain the photoelectric conversion layer. Optionally, during this process the A³-containing precursor may be further supplied in a gas phase. In this case, the third perovskite compound represented by Formula 3 may be polycrystalline.

[0117] Next, a hole blocking layer 540 may be provided on the photoelectric conversion layer 530. The hole blocking layer 540 may include a second perovskite compound represented by Formula 2. The second perovskite compound represented by Formula 2 may be obtained from a second mixture including an A²-containing precursor, a B²-containing precursor, and a solvent.

[0118] The hole blocking layer 540 may further include a polymer, together with the second perovskite compound. In this regard, the second mixture may further include the polymer or a precursor thereof.

[0119] The polymer may be any of a variety of polymers. The polymer may be a polar polymer that may be soluble and miscible with the second perovskite compound in a solvent. For example, the polar polymer may be polyamic acid, polyimide, polyvinyl alcohol (PVA), polyacrylic acid, polyhydroxyethyl methacrylate (PHEMA), polymethyl methacrylate (PMMA), polyacrylate, or polyacrylonitrile (PAN). However, example embodiments are not limited thereto. The polymer may include a copolymer of the above-listed polymer materials.

[0120] For example, the second mixture may be spin-coated on the photoelectric conversion layer 530. When the second mixture is applied onto the photoelectric conversion layer 530 by spin coating, appropriate spin coating conditions

may be chosen from, for example, a coating rate range of about 2,000 rpm to about 4,000 rpm and a temperature range of about 80°C to about 200°C, in consideration of the composition of the second mixture and the structure of the hole blocking layer 540.

[0121] The second mixture may be applied onto the photoelectric conversion layer 530 by using any of a variety of methods known in the art.

[0122] The second mixture applied onto the photoelectric conversion layer 530 may be thermally treated to form the hole blocking layer 540. The thermal treatment temperature may be in a range of about 100°C to about 300°C. When the thermal treatment temperature is less than 100°C, the hole blocking layer 540 may have reduced adhesion. When the thermal treatment temperature exceeds 300°C, the second perovskite compound may be damaged.

[0123] For example, appropriate thermal treatment conditions may be chosen from a temperature range of about 100°C to about 300°C for about 15 minutes to about 2 hours in consideration of the composition of the second mixture and the structure of the hole blocking layer 540.

[0124] The hole blocking layer 540 formed as described above may include the second perovskite compound. For example, the hole blocking layer 540 may include the second perovskite compound and the polar polymer, and in some embodiments, a composite of the second perovskite compound and the polar polymer, and in some other embodiments, two separate layers including the second perovskite compound and the polar polymer, respectively.

[0125] In the A²-containing precursor and the B²-containing precursor, A² and B² may be defined the same as described above in connection with Formula 2.

[0126] For example, the A²-containing precursor may be selected from halides of A² (for example, (A²)(X²)), and the B²-containing precursor may be selected from halides of B² (for example, (B²)(Y²)₂). In the (A²)(X²) and (B²)(Y²)₂, A², B², X², and Y² may be defined the same as described above in connection with Formula 2.

[0127] The solvent may be selected from the materials in which the A²-containing precursor and the B²-containing precursor have high solubility. For example, the solvent may be dimethylformamide, dimethyl sulfoxide, γ -butyrolactone, N-methyl-2-pyrrolidone, or any combination thereof. However, example embodiments are not limited thereto.

[0128] Next, a second conductive layer 550 may be provided on the hole blocking layer 540. The second conductive layer 550 may be the same as the second conductive layer 150 described above with reference to FIG. 1. The second conductive layer 550 may be provided using any of a variety of methods known in the art, and thus, a detailed description thereof will be omitted here.

[0129] A photoelectric conversion device according to any of the above-described example embodiments may be included in an imaging device. The imaging device may be a stationary or mobile imaging device.

[0130] The imaging device may include a light irradiation unit, a photodetector unit, and a control unit.

[0131] The light irradiation unit may include a light source which generates light, and a collimator which guides a path of the generated light to control a light irradiation region.

[0132] The light source may include, for example, an X-ray tube. The X-ray tube may be implemented as a bipolar vacuum tube consisting of a cathode and an anode. A voltage applied between the cathode and the anode of the X-ray tube is referred to as a tube voltage, wherein the maximum tube voltage is expressed in peak kilovoltage (kVp). An increased tube voltage leads to an increased rate of thermoelectrons, which consequently leads to increased X-ray energy (photon energy) from collision of thermoelectrons against a target material. A current which flows in the X-ray tube is referred to as a tube current, and an average tube current is expressed in mA. An increased tube current leads to an increased number of thermoelectrons emitted from the filament, which consequently leads to an increased X-ray dose (number of X-ray photons) from collision of thermoelectrons against a target material. Thus, X-ray energy may be controlled by the tube voltage, and the X-ray intensity or dose may be controlled by the tube current and an X-ray exposure time.

[0133] The photodetector unit may detect light which has passed through an object after emission from the light irradiation unit. For example, the photodetector unit may include a flat photodetector. The photodetector unit may include the photoelectric conversion device 100 described above with reference to FIG. 1.

[0134] The control unit may include a voltage generating unit, a signal processing unit, and an operating unit, and may control the overall operation of the imaging device.

[0135] The voltage generating unit may generate a high voltage for light emission and apply the voltage to the light source of the light irradiation unit.

[0136] The signal processing unit may generate an image by processing information detected by the photodetector unit or may generate a control signal based on information input to the operating unit to control the components of the imaging device.

[0137] The operating unit, which may provide an interface for operating the imaging device, may receive various types of information, regarding operation commands of the image device or imaging, from a user.

[0138] The imaging device may further include an output unit. The output unit may display imaging-related information such as light irradiation or may display an image generated by the signal processing unit.

[0139] One or more example embodiments of the present disclosure will now be described in detail with reference to

the following examples. However, these examples are only for illustrative purposes and are not intended to limit the scope of the one or more example embodiments of the present disclosure. In the following preparation examples, the expression that " 'B' was used, instead of 'A' " means that the amounts of 'B' and 'A' were the same in equivalent amounts.

[Examples]

Preparation Example 1. Preparation of electron blocking material (mixture B)

(1) Preparation of mixture A

[0140] After p-phenylenediamine and biphenyl-tetracarboxylic acid dianhydride were mixed in a molar ratio of about 1:0.975 in a reactor, N-methyl-2-pyrrolidone (NMP) was added to the mixture and stirred under nitrogen atmosphere at room temperature for about 5 hours. Then, the resulting mixture was reacted in an airtight reactor at about 40°C for about 12 hours to prepare mixture A.

(2) Preparation of mixture B

[0141] 1.59 g of $\text{CH}_3\text{NH}_3\text{I}$, 4.61g of PbI_2 , and 2.4 g of dimethylformamide were added to 4.8 g of the mixture A and stirred overnight at room temperature to prepare mixture B.

Preparation Example 2. Preparation of hole blocking material (mixture C, mixture D, or mixture E)

2-1. Preparation of mixture C

[0142] $\text{CH}_3\text{NH}_3\text{Br}$, PbBr_2 , dimethyl formamide, and dimethyl sulfoxide were mixed in a molar ratio of about 1:1:6.7:2 in a reactor, and stirred at room temperature for about 1 hour to prepare mixture C.

2-2. Preparation of mixture D

(1) Preparation of mixture A

[0143] p-phenylenediamine and biphenyl-tetracarboxylic acid dianhydride were mixed in a molar ratio of about 1:0.975 in a reactor, NMP was added to the mixture and stirred under nitrogen atmosphere at room temperature for about 5 hours. Then, the resulting mixture was reacted in an airtight reactor at about 40°C for about 12 hours to prepare mixture A.

(2) Preparation of mixture D

[0144] 2.34 g of $\text{CH}_3\text{NH}_3\text{Br}$, 7.67 g of PbBr_2 , and 4.8 g of dimethylformamide were added to 9.6 g of the mixture A and stirred overnight at room temperature to prepare mixture D.

2-3. Preparation of mixture E

[0145] Mixture E was prepared in the same manner as above in Section 2-2 of Preparation Example 2, except that 1.17 g of $\text{CH}_3\text{NH}_3\text{Br}$ and 3.835 g of PbBr_2 were used instead of 2.34 g of $\text{CH}_3\text{NH}_3\text{Br}$ and 7.67 g of PbBr_2 .

Preparation Example 3. Preparation of photoelectric conversion material (mixture F or mixture G)

3-1. Preparation of mixture F

[0146] $\text{CH}_3\text{NH}_3\text{I}$, PbI_2 , dimethyl formamide, and dimethyl sulfoxide were added to a reactor in a molar ratio of about 1:1:6.7:2, and stirred at room temperature for about 1 hour to prepare mixture F.

3-2. Preparation of mixture G

[0147] After 18.44 g of PbI_2 and 7.75 g of γ -butyrolactone were mixed in a reactor and stirred at about 80°C for about 1 hour, 6.36 g of $\text{CH}_3\text{NH}_3\text{I}$ was further added to the mixture and stirred at about 90°C to about 100°C for about 4 hours. Then, 4 g of α -terpinol was further added to the mixture and stirred at about 90°C to about 100°C for about 4 hours to prepare mixture G.

Example 1. Manufacture of photoelectric conversion device

[0148] A first conductive layer having a thickness of about 200 nm was formed by sputtering amorphous ITO onto a glass substrate.

[0149] The mixture B was spin-coated on the first conductive layer at about 2,000 rpm for about 30 seconds, and dried at about 120°C for about 30 minutes to form an electron blocking layer having a thickness of about 3 μm .

[0150] The mixture G was coated on the electron blocking layer using a doctor blade, thermally treated at about 120°C for about 1 hour, and then thermally treated in a vacuum oven at about 90°C for about 1 hour, thereby forming a preliminary photoelectric conversion layer. The preliminary photoelectric conversion layer was pressed under 5 atm at about 120°C to form a photoelectric conversion layer having a thickness of about 830 μm .

[0151] The mixture C was spin-coated on the photoelectric conversion layer at about 2,000 rpm for about 30 seconds, while about 2 mL of diethyl ether was dropwise added each second for about 20 seconds, starting from about 10 seconds after the start of the spin coating, followed by heat treatment at about 100°C for about 10 minutes to form a hole blocking layer having a thickness of about 1 μm .

[0152] A glass substrate including amorphous ITO sputtered thereonto to a thickness of about 200 nm was combined onto the hole blocking layer, thereby manufacturing a photoelectric conversion device.

[0153] Surface images of the electron blocking layer, the photoelectric conversion layer, and the hole blocking layer in Example 1 are shown in FIGS. 6A to 6C, respectively. Scanning electron microscope (SEM) images of the electron blocking layer, the photoelectric conversion layer, and the hole blocking layer in the photoelectric conversion device of Example 1 are shown in FIG.11, FIGS. 12A to 12C, and FIG.13.

Example 2. Manufacture of photoelectric conversion device

[0154] A photoelectric conversion device was manufactured in the same manner as in Example 1, except that the mixture D, instead of the mixture C, was used to form the hole blocking layer.

[0155] SEM images of the hole blocking layer in the photoelectric conversion device of Example 2 are shown in FIGS. 14A and 14B. Referring to FIGS. 14A and 14B, a square star pattern was found on the surface of the hole blocking layer.

Example 3. Manufacture of photoelectric conversion device

[0156] A photoelectric conversion device was manufactured in the same manner as in Example 1, except that mixture E, instead of mixture C, was used to form the hole blocking layer.

Comparative Example 1. Manufacture of photoelectric conversion device

[0157] A photoelectric conversion device was manufactured in the same manner as in Example 1, except that the hole blocking layer and the electron blocking layer were not included.

Comparative Example 2. Manufacture of photoelectric conversion device

[0158] A photoelectric conversion device was manufactured in the same manner as in Example 1, except that TiO_2 was used, instead of the mixture C, to form the hole blocking layer, and spiro-OMeTAD(2,2',7,7'-tetrakis(N,N-dimethoxyphenyl-amine)9,9'-spiro-bifluorene), instead of the mixture B, was used to form the electron blocking layer.

Comparative Example 3. Manufacture of photoelectric conversion device

[0159] A photoelectric conversion device was manufactured in the same manner as in Example 1, except that the mixture A, instead of the mixture B, was used to form the electron blocking layer.

Comparative Example 4. Manufacture of photoelectric conversion device

[0160] A photoelectric conversion device was manufactured in the same manner as in Example 1, except that the mixture A, instead of the mixture B, was used to form the electron blocking layer, and the drying was performed at about 200°C, instead of about 120°C.

Comparative Example 5. Manufacture of photoelectric conversion device

[0161] A photoelectric conversion device was manufactured in the same manner as in Example 1, except that the

hole blocking layer and the electron blocking layer were not included, and a photoelectric conversion layer having a thickness of about 0.5 μm was formed by coating the mixture F by spin coating, instead of coating the mixture G by doctor blade coating.

Evaluation Example 1

[0162] Current densities of the photoelectric conversion devices of Examples 1 to 3 and Comparative Examples 1 and 2 were measured at different voltages. The measurement of the current densities was repeated under the same conditions with and without external light irradiation ("Photo" and "Dark" conditions, respectively). The experimental results are shown in FIG. 7.

[0163] Referring to FIG. 7, the photoelectric conversion devices of Examples 1 to 3 were found to have a lower dark current as compared with the photoelectric conversion devices of Comparative Examples 1 and 2.

Evaluation Example 2

[0164] Current densities of the photoelectric conversion devices of Comparative Examples 3 and 4 were measured at different voltages. The measurement of the current densities was repeated under the same conditions with and without external light irradiation ("Photo" and "Dark" conditions, respectively). The experimental results are shown in FIG. 8.

[0165] Referring to FIG. 8, the photoelectric conversion devices of Comparative Examples 3 and 4 were found to be significantly reduced both in photocurrent and dark current, due to the use of polyimide only in the electron blocking layer. In particular, in the photoelectric conversion device of Comparative Example 4, a remarkable reduction in photocurrent as well as in dark current was found due to the imidization. This is attributed to that when the mixture A, instead of the mixture B, was used to form the electron blocking layer, the produced polyimide served as a barrier of photocharge transfer to an electrode.

Evaluation Example 3

[0166] Currents of the photoelectric conversion device of Example 2 were measured at different voltages. The photoelectric conversion device was irradiated by X-rays, wherein a distance between an X-ray source and the photoelectric conversion device was about 30 cm, an X-ray tube voltage was about 100 kVp, an X-ray tube current was about 20 mA, and an X-ray irradiation time was about 0.2 seconds. The experimental results are shown in FIG. 9.

[0167] Referring to FIG. 9, the photoelectric conversion device of Example 2 was found to have a high sensitivity to X-rays.

Evaluation Example 4

[0168] Photoabsorption spectra and photoluminescence intensities with respect to time of the photoelectric conversion layers in the photoelectric conversion devices of Comparative Examples 1 and 5 were evaluated. The results are shown in FIGS. 10A and 10B, respectively. A light source having a wavelength of 505 nm was used as an excitation source, and the carrier lifetime τ was determined using time-resolved photoluminescence (TRPL).

[0169] Referring to FIG. 10A, the photoelectric conversion layer of Comparative Example 5 was found to exhibit an absorption edge at about 760 nm, while the photoelectric conversion layer of Comparative Example 1 exhibited an expanded absorption band at about 840 nm.

[0170] Referring to FIG. 10B, the photoelectric conversion layer of Comparative Example 5 had a carrier lifetime (τ) of about 128 ns, while the photoelectric conversion layer of Comparative Example 1 had a carrier lifetime (τ) of about 1,052 ns.

[0171] Also, the photoelectric conversion device of Comparative Example 1 exhibited a higher photoluminescent intensity by about 100 times than the photoelectric conversion device of Comparative Example 5.

[0172] This result supports that the photoelectric conversion layer having a thickness of about hundreds of micrometers or greater formed by doctor blade-coating the mixture G may exhibit improved photoelectric conversion efficiency than the photoelectric conversion layer having a thickness of several micrometers formed by spin-coating the mixture F.

[0173] As described above, according to the one or more example embodiments, a photoelectric conversion device including a perovskite compound may have improved photoelectric conversion efficiency and a reduced dark current, and a high-definition imaging device may be provided by using the photoelectric conversion device.

[0174] It should be understood that example embodiments described herein should be considered in a descriptive sense only and not for purposes of limitation. Descriptions of features or aspects within each embodiment should typically be considered as available for other similar features or aspects in other example embodiments.

[0175] While one or more example embodiments have been described with reference to the figures, it will be understood

by those of ordinary skill in the art that various changes in form and details may be made therein without departing from the scope as defined by the following claims.

Claims

1. A photoelectric conversion device comprising:

a first conductive layer;
 a second conductive layer;
 a photoelectric conversion layer between the first conductive layer and the second conductive layer;
 an electron blocking layer between the photoelectric conversion layer and the first conductive layer; and
 a hole blocking layer between the photoelectric conversion layer and the second conductive layer,
 wherein the electron blocking layer comprises a first perovskite compound represented by Formula 1, and the
 hole blocking layer comprises a second perovskite compound represented by Formula 2:



wherein, in Formula 1,

A¹ is at least one monovalent organic cation, at least one monovalent inorganic cation, or any combination thereof,
 B¹ is at least one divalent inorganic cation,
 X¹ and Y¹ are each independently at least one monovalent anion, and
 n is a real number satisfying $0 \leq n \leq 3$, and



wherein, in Formula 2,

A² is at least one monovalent organic cation, at least one monovalent inorganic cation, or any combination thereof,
 B² is at least one divalent inorganic cation,
 X² and Y² are each independently at least one monovalent anion, and
 m is a real number satisfying $0 \leq m \leq 3$.

2. The photoelectric conversion device of claim 1, wherein A¹ and A² are each independently selected from (R₁R₂R₃R₄N)⁺, (R₁R₂R₃R₄P)⁺, (R₁R₂R₃R₄As)⁺, (R₁R₂R₃R₄Sb)⁺, (R₁R₂N=C(R₃)-NR₄R₅)⁺, a substituted or unsubstituted cycloheptatrienium, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Fr⁺, and any combination thereof; and R₁ to R₅, and at least one substituent of the substituted cycloheptatrienium are each independently selected from hydrogen, deuterium, -F, -Cl, -Br, -I, a hydroxyl group, a C₁-C₂₀ alkyl group, a C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl group, a C₁-C₂₀ alkoxy group, and -N(Q₁)(Q₂), and Q₁ and Q₂ are each independently be selected from hydrogen, deuterium, a C₁-C₂₀ alkyl group, a C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl group, and a C₁-C₂₀ alkoxy group; and/or wherein A¹ and A² are each independently selected from (CH₃NH₃)⁺, ((CH₃CH₂CH₂CH₂)NH₃)⁺, (NH₂CHNH₂)⁺, K⁺, Rb⁺, Cs⁺, and any combination thereof.

3. The photoelectric conversion device of claims 1 or 2, wherein B¹ and B² are each independently selected from La²⁺, Ce²⁺, Pr²⁺, Nd²⁺, Pm²⁺, Sm²⁺, Eu²⁺, Gd²⁺, Tb²⁺, Dy²⁺, Ho²⁺, Er²⁺, Tm²⁺, Yb²⁺, Lu²⁺, Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Ra²⁺, Pb²⁺, Sn²⁺, and any combination thereof; preferably wherein B¹ and B² are Pb²⁺.

4. The photoelectric conversion device of any of claims 1-3, wherein X¹, Y¹, X², and Y² each independently are selected from Cl⁻, Br⁻, and I⁻; and/or wherein the first perovskite compound represented by Formula 1 and the second perovskite compound represented by Formula 2 each independently are selected from CH₃NH₃PbI₃, CH₃NH₃PbBr₃, CH₃NH₃PbCl₃,

$\text{CH}_3\text{NH}_3\text{PbBr}_{(3-o)\text{I}_o}$, $\text{CH}_3\text{NH}_3\text{PbCl}_{(3-o)\text{Br}_o}$, $\text{CH}_3\text{NH}_3\text{PbCl}_{(3-o)\text{I}_o}$, CsPbI_3 , CsPbBr_3 , $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3\text{PbBr}_3$, $\text{NH}_2\text{CHNH}_2\text{PbBr}_3$, $\text{NH}_2\text{CHNH}_2\text{PbBr}_{(3-o)\text{I}_o}$, $[\text{CH}_3\text{NH}_3]_{(1-x)}[\text{NH}_2\text{CHNH}_2]_x\text{PbBr}_3$, and $[\text{CH}_3\text{NH}_3]_{(1-x)}[\text{NH}_2\text{CHNH}_2]_x\text{PbBr}_{(3-o)\text{I}_o}$, wherein o is a real number greater than 0 and less than 3, and x is a real number greater than 0 and less than 1.

- 5 5. The photoelectric conversion device of any of claims 1-4, wherein the electron blocking layer and the hole blocking layer each independently further comprises a polar polymer.
6. The photoelectric conversion device of claim 5, wherein an amount of the polar polymer in the electron blocking layer is 5 parts to 60 parts by weight with respect to 100 parts by weight of the first perovskite compound represented by Formula 1, and
 10 an amount of the polar polymer in the hole blocking layer is 5 parts to 60 parts by weight with respect to 100 parts by weight of the second perovskite compound represented by Formula 2; and/or
 wherein the polar polymer is selected from polyamic acid, polyimide, polyvinyl alcohol (PVA), polyacrylic acid, polyhydroxyethyl methacrylate (PHEMA), polymethyl methacrylate (PMMA), polyacrylate, polyacrylonitrile (PAN),
 15 and any combination thereof.
7. The photoelectric conversion device of any of claims 1-6, wherein the electron blocking layer comprises $\text{CH}_3\text{NH}_3\text{PbI}_3$ and polyimide, and the hole blocking layer comprises $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and polyimide;
 20 preferably wherein the hole blocking layer has a square star pattern, a butterfly pattern, a starfish pattern, a sawtooth pattern, or a clover pattern on a surface thereof.
8. The photoelectric conversion device of any of claims 1-7, wherein the photoelectric conversion layer comprises a photoactive material,
 the lowest unoccupied molecular orbital (LUMO) energy level of the photoactive material is equal to or lower than
 25 the LUMO energy level of the first perovskite compound, and
 the highest occupied molecular orbital (HOMO) energy level of the photoactive material is greater than or equal to the HOMO energy level of the second perovskite compound; and/or
 wherein the photoelectric conversion layer comprises a third perovskite compound represented by Formula 3, and the third perovskite compound is polycrystalline:
 30

$$\text{<Formula 3> } [\text{A}^3][\text{B}^3][\text{X}^3_{(3-k)}\text{Y}^3_k]$$
 wherein, in Formula 3,
 35 A^3 is at least one monovalent organic cation, at least one monovalent inorganic cation, or any combination thereof,
 B^3 is at least one divalent inorganic cation,
 X^3 and Y^3 are each independently at least one monovalent anion, and
 k is a real number satisfying $0 \leq k \leq 3$.
 40
9. The photoelectric conversion device of claim 8, wherein crystals of the third perovskite compound represented by Formula 3 are fused to each other; and/or
 wherein a longest axis of the third perovskite compound represented by Formula 3 has a length of 1 μm to 300 μm ; and/or
 45 wherein the third perovskite compound represented by Formula 3 is $\text{CH}_3\text{NH}_3\text{PbI}_3$.
10. The photoelectric conversion device of any of claims 1-9, wherein the photoelectric conversion layer absorbs infrared rays, visible rays, or X-rays; and/or
 wherein the photoelectric conversion layer has a thickness of 0.1 μm to 1,500 μm .
 50
11. The photoelectric conversion device of any of claims 1-10, wherein the second conductive layer is reflective, transmissive, or semi-transmissive.
12. A method of manufacturing a photoelectric conversion device, the method comprising:
 55 forming a first conductive layer;
 forming an electron blocking layer comprising a first perovskite compound represented by Formula 1 on the first conductive layer;

forming a photoelectric conversion layer on the electron blocking layer;
 forming a hole blocking layer comprising a second perovskite compound represented by Formula 2 on the photoelectric conversion layer; and
 forming a second conductive layer on the hole blocking layer;



wherein, in Formula 1,

A¹ is at least one monovalent organic cation, at least one monovalent inorganic cation, or any combination thereof,
 B¹ is at least one divalent inorganic cation,
 X¹ and Y¹ are each independently at least one monovalent anion, and
 n is a real number satisfying $0 \leq n \leq 3$, and



wherein, in Formula 2,

A² is at least one monovalent organic cation, at least one monovalent inorganic cation, or any combination thereof,
 B² is at least one divalent inorganic cation,
 X² and Y² are each independently at least one monovalent anion, and
 m is a real number satisfying $0 \leq m \leq 3$.

13. The method of claim 12, wherein the electron blocking layer and the hole blocking layer each independently further comprises a polar polymer; and/or
 wherein the forming of the electron blocking layer comprises: spin-coating a mixture of a precursor of the first perovskite compound represented by Formula 1 and a polar polymer or a precursor thereof onto the first conductive layer, and thermally treating a resulting structure at 100°C to 300°C.

14. The method of claims 12 or 13, wherein the forming of the photoelectric conversion layer comprises:

(a) adding a non-solvent to a mixture including a A³-containing precursor, a B³-containing precursor and a solvent and stirring at a temperature of 70°C to 120°C to prepare a solution of a third perovskite compound represented by Formula 3; and
 (b) coating the solution of the third perovskite compound on the electron blocking layer by doctor blade coating or bar coating:



wherein, in Formula 3,

A³ is at least one monovalent organic cation, at least one monovalent inorganic cation, or any combination thereof,
 B³ is at least one divalent inorganic cation,
 X³ and Y³ are each independently at least one monovalent anion, and
 k is a real number satisfying $0 \leq k \leq 3$,

the solvent is dimethylformamide, dimethyl sulfoxide, γ -butyrolactone, or any combination thereof, and
 the non-solvent is α -terpineol, hexyl carbitol, butyl carbitol acetate, hexyl cellosolve, butyl cellosolve acetate, or any combination thereof.

15. An imaging device comprising a light irradiation unit, a photodetector unit, and a control unit, the photodetector unit comprising the photoelectric conversion device of any of claims 1 to 11.

FIG. 1

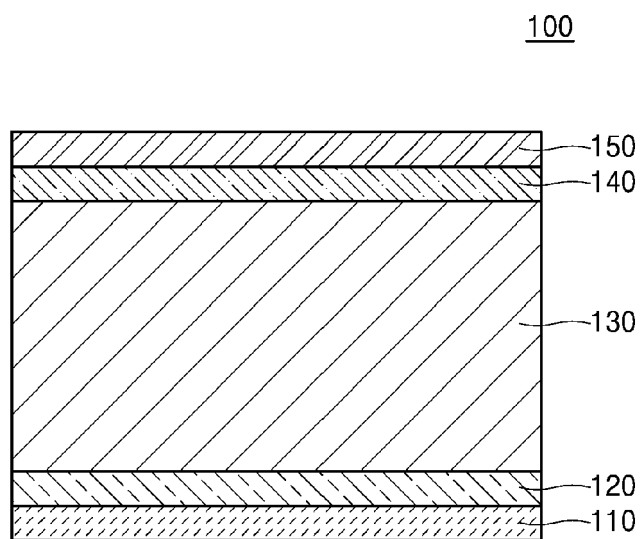


FIG. 2A

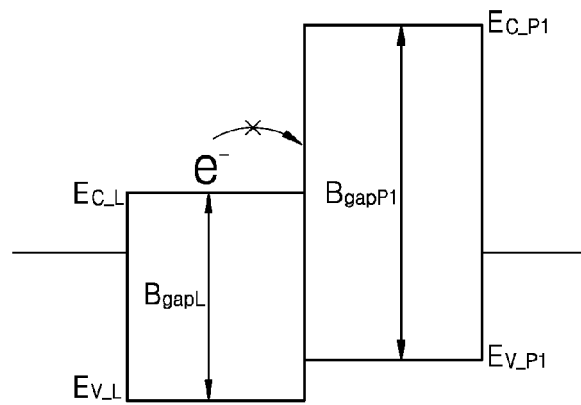


FIG. 2B

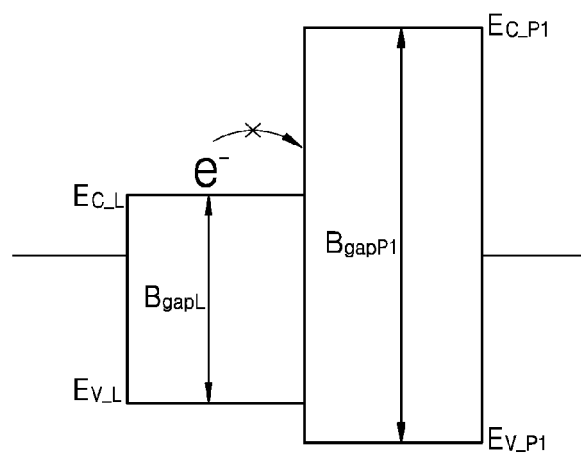


FIG. 3A

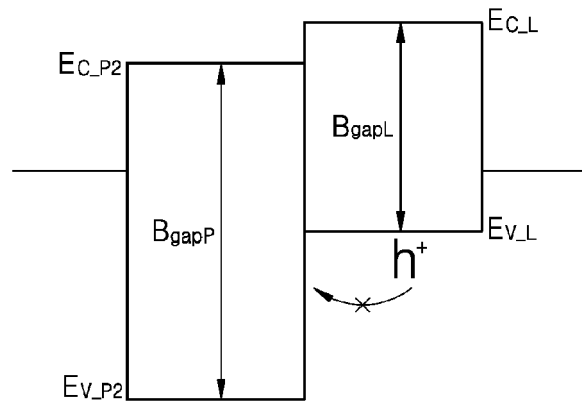


FIG. 3B

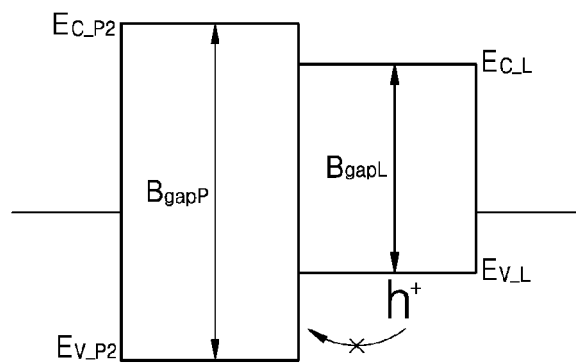


FIG. 4

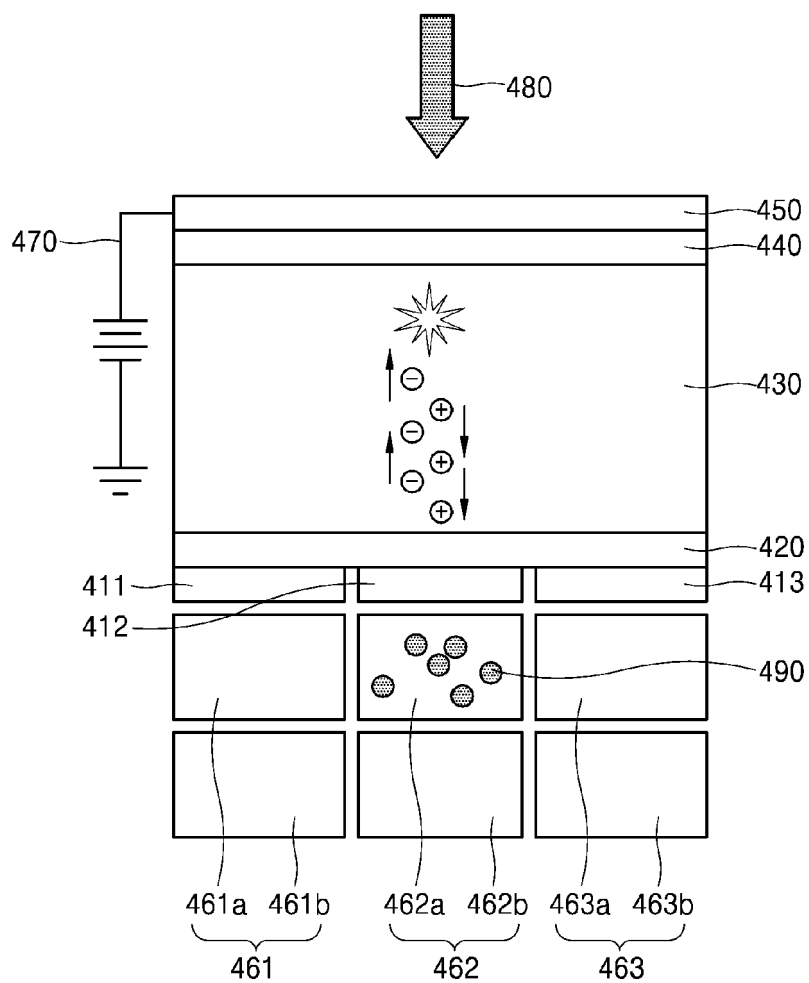


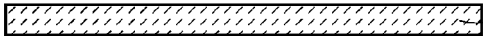
FIG. 5A  510

FIG. 5B  520
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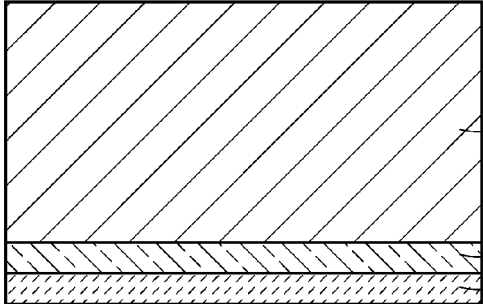
FIG. 5C  530
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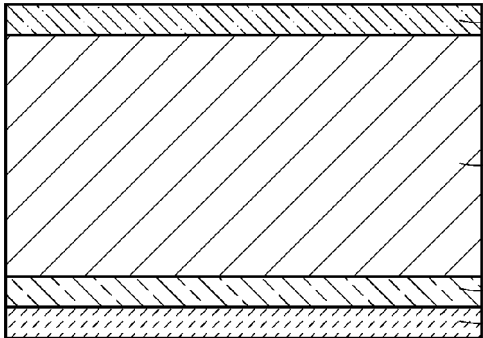
FIG. 5D  540
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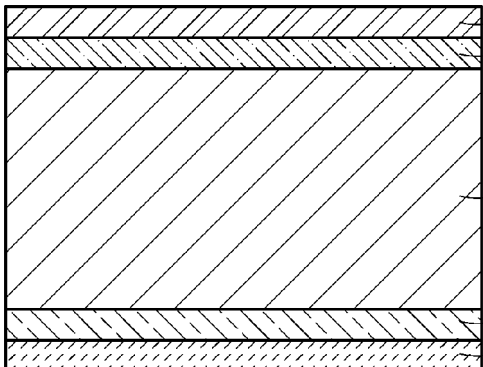
FIG. 5E  550
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FIG. 6A

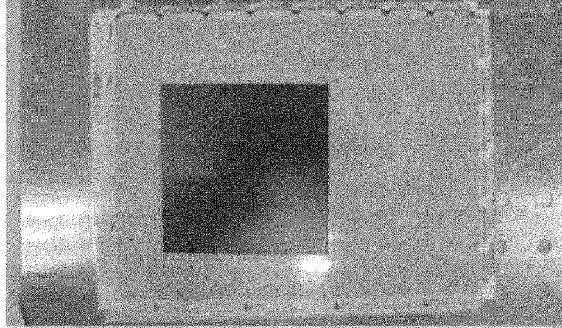


FIG. 6B

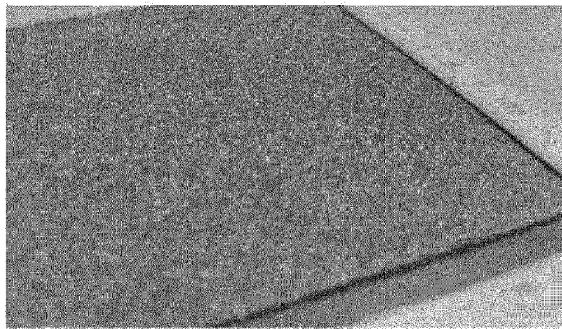


FIG. 6C

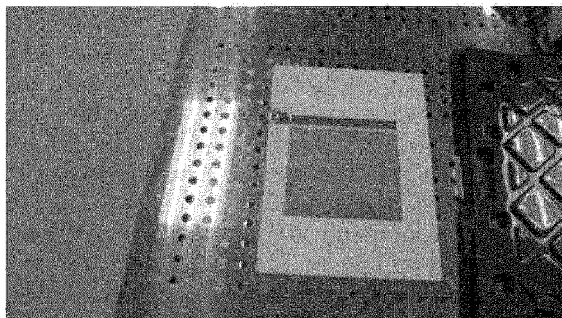


FIG. 7

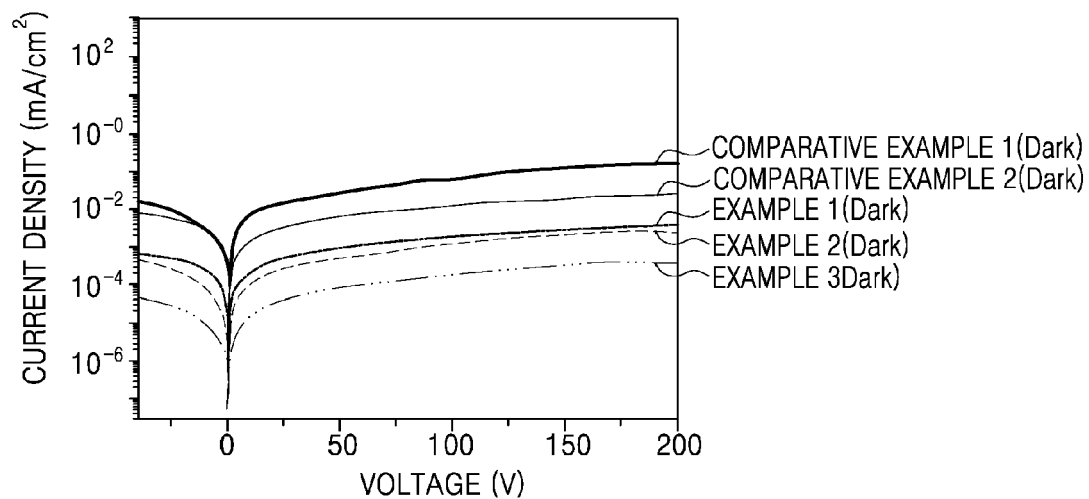


FIG. 8

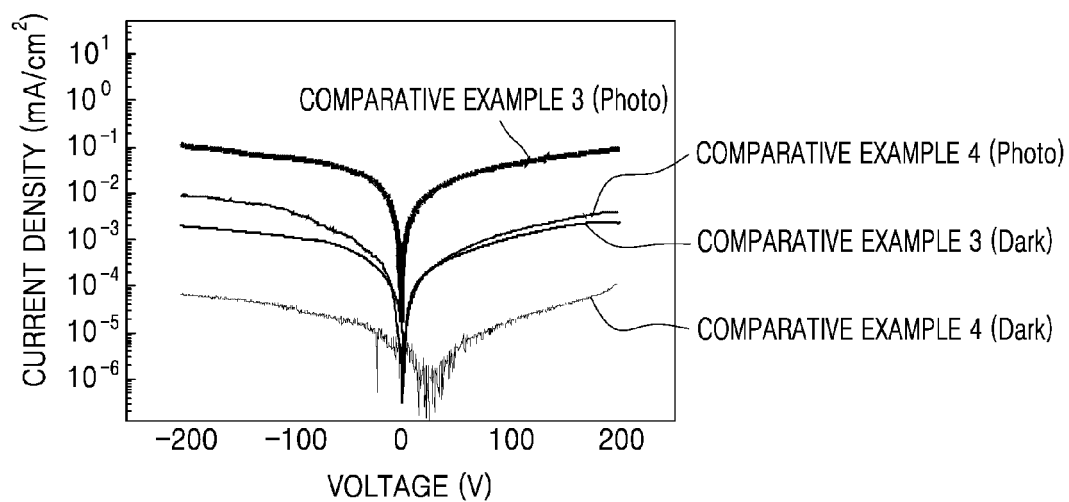


FIG. 9

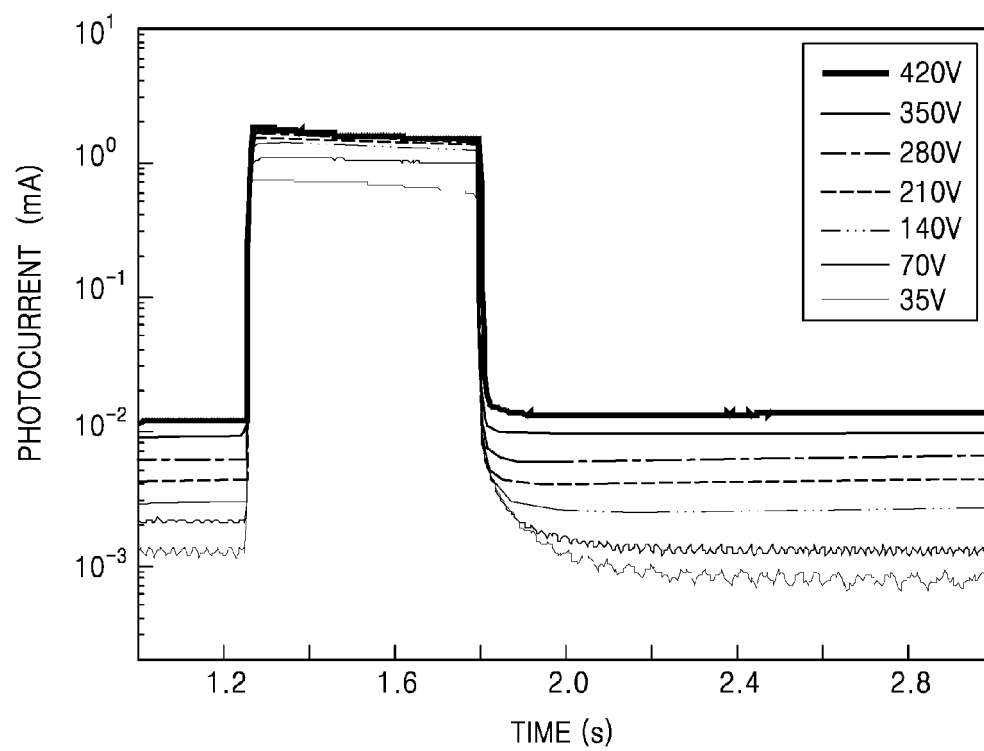


FIG. 10A

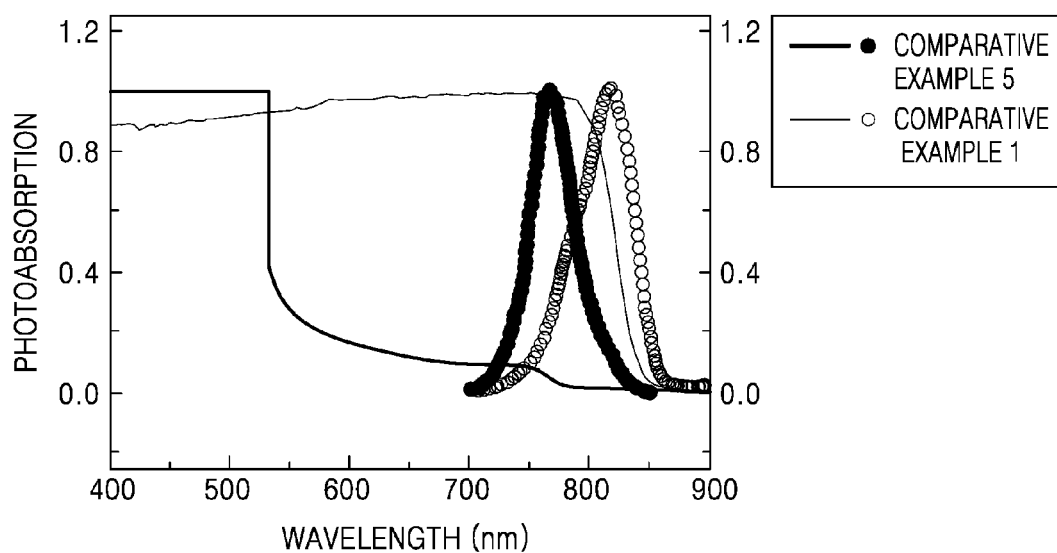


FIG. 10B

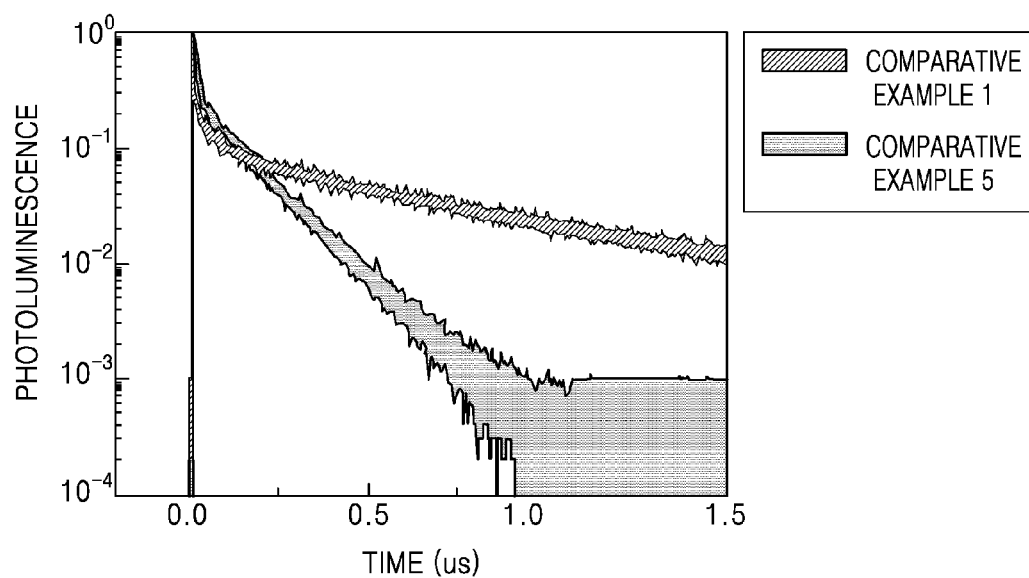


FIG. 11

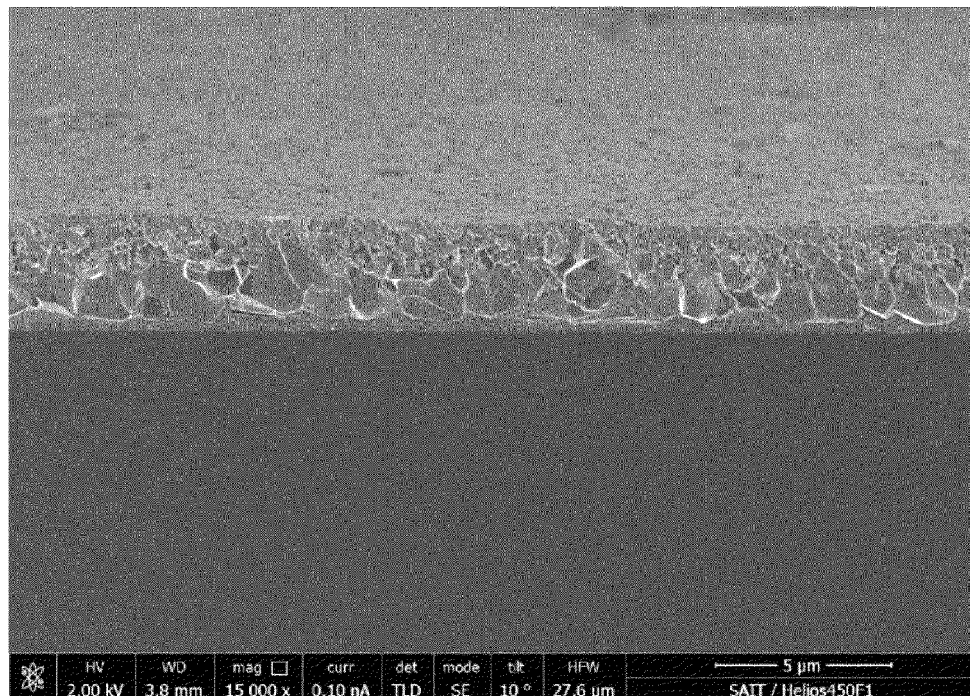


FIG. 12A

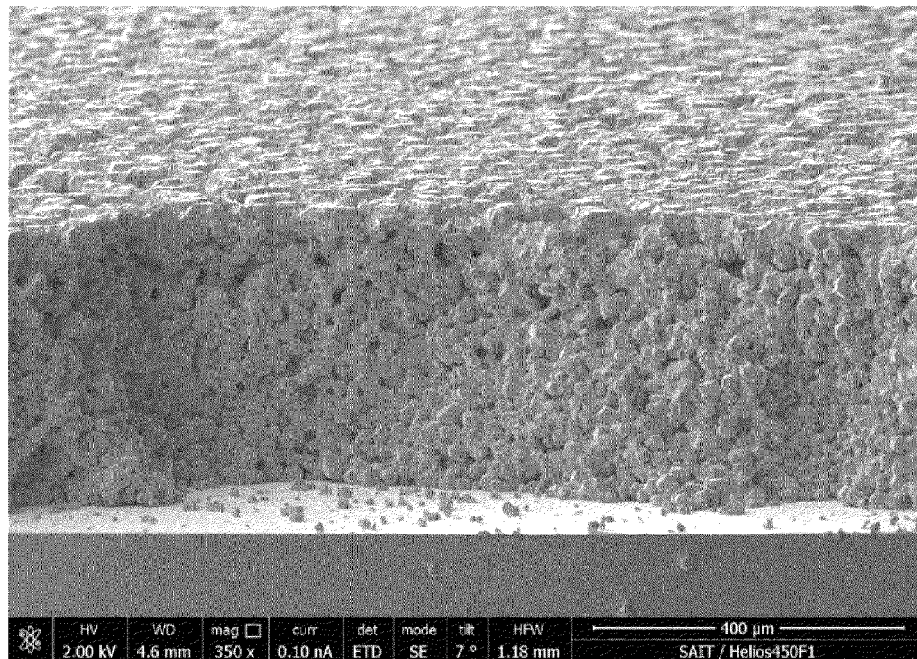


FIG. 12B

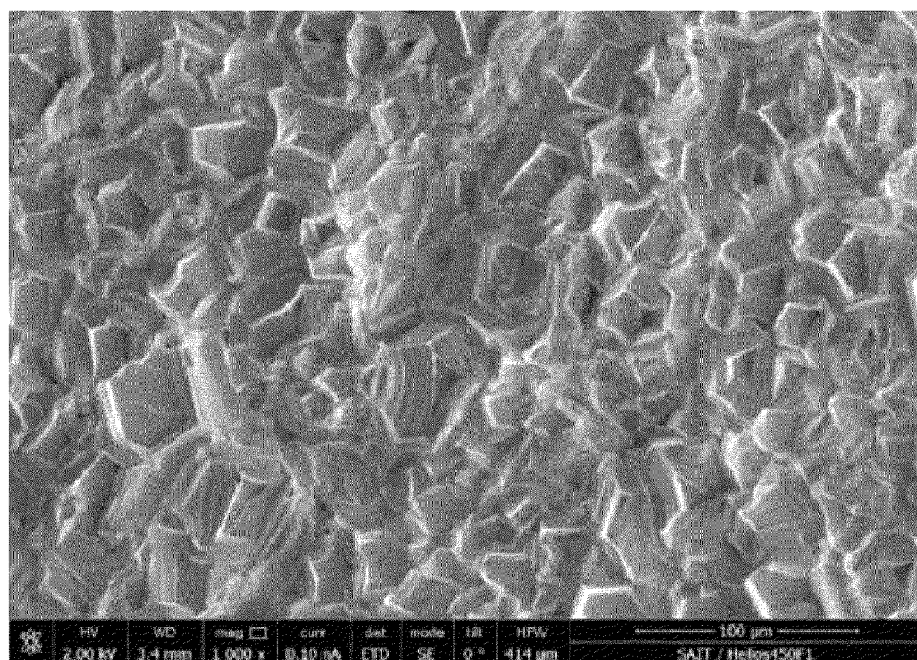


FIG. 12C

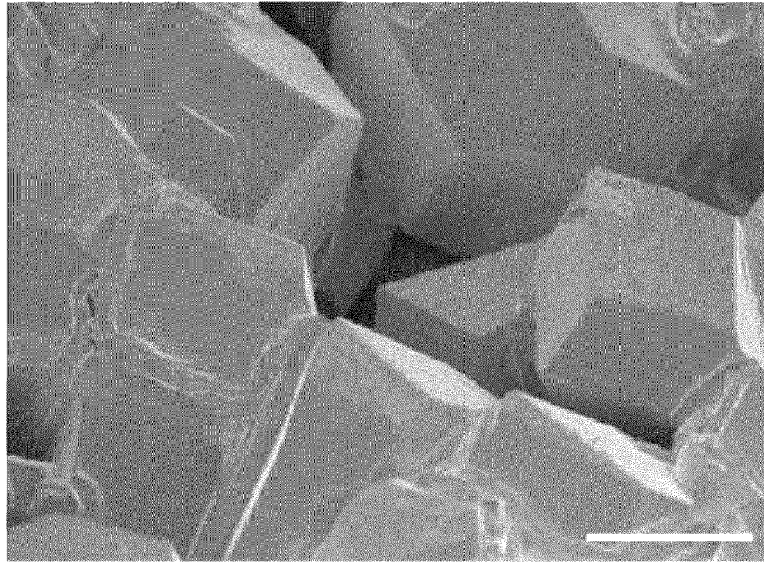


FIG. 13

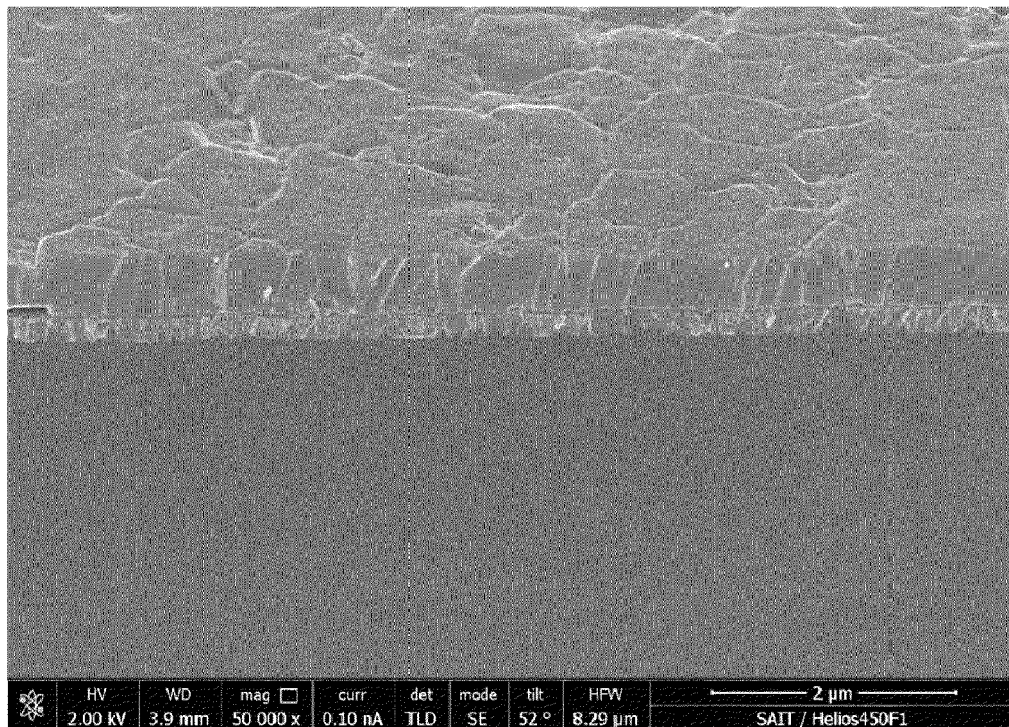


FIG. 14A

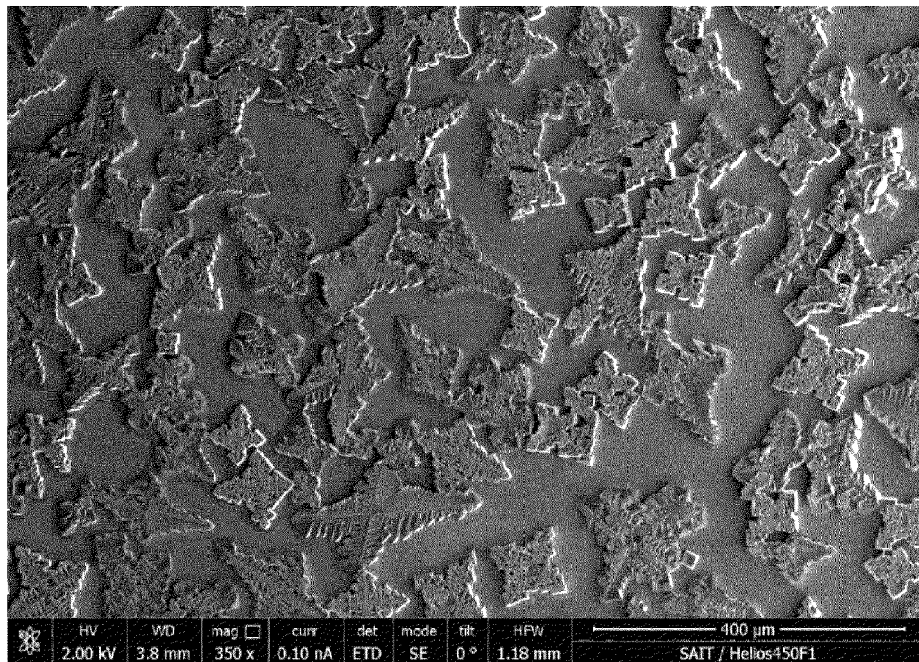
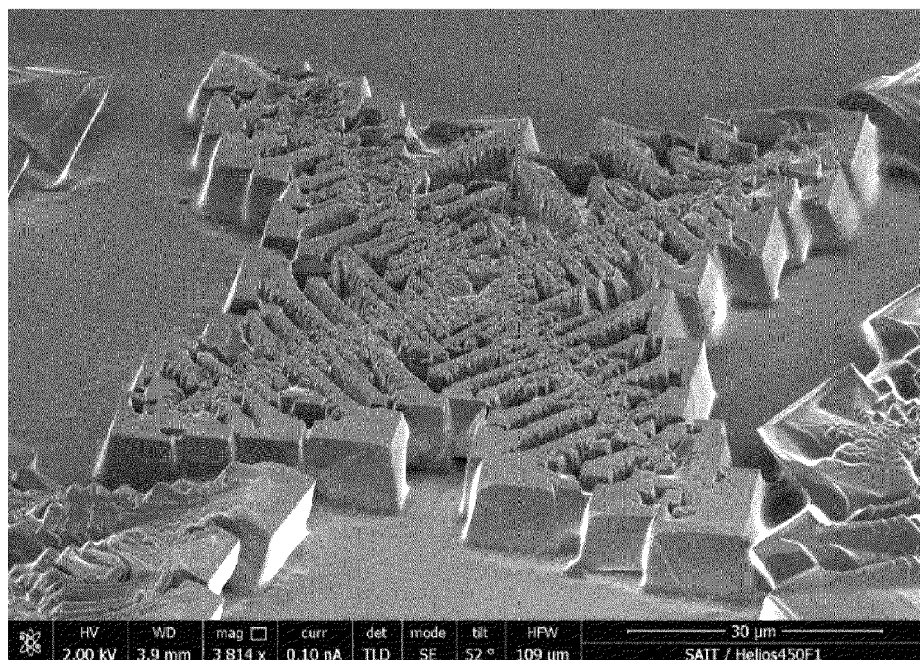


FIG. 14B





EUROPEAN SEARCH REPORT

Application Number
EP 18 16 1006

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Y	* paragraph [0054] - paragraph [0065]; figures 1,2 *	5-7	
Y	* paragraph [0008] - paragraph [0049] *	5-7	
Y	WO 2016/115602 A1 (COMMW SCIENT IND RES ORG [AU]) 28 July 2016 (2016-07-28) * paragraph [0138] - paragraph [0142]; example 5 * * paragraph [0120] - paragraph [0122] *	5-7	
A	EP 2 846 371 A1 (ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE EPFL [CH]; UNIV VALENCIA [ES]) 11 March 2015 (2015-03-11) * paragraph [0031] - paragraph [0098]; figures 1,2 *	1-15	TECHNICAL FIELDS SEARCHED (IPC) H01L
A	OLGA MALINKIEWICZ ET AL: "Perovskite solar cells employing organic charge-transport layers", NATURE PHOTONICS, 22 December 2013 (2013-12-22), XP055097137, ISSN: 1749-4885, DOI: 10.1038/nphoton.2013.341 * the whole document *	1-15	
A	PHILIP SCHULZ ET AL: "Interface energetics in organo-metal halide perovskite-based photovoltaic cells", ENERGY & ENVIRONMENTAL SCIENCE, vol. 7, no. 4, 13 February 2014 (2014-02-13), pages 1377-1381, XP055367276, Cambridge ISSN: 1754-5692, DOI: 10.1039/c4ee00168k * page 1377 - page 1380; figures 1,3 *	1-15	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 22 August 2018	Examiner Konrádsson, Ásgeir
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 18 16 1006

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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22-08-2018

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